

## Oxidative Coupling of Methane over Transition-Metal-Substituted Strontium Hydroxyapatite

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**Abstract**—Lead-substituted strontium hydroxyapatite ( $\text{Sr}_{10-x}\text{Pb}_x(\text{OH})_2(\text{PO}_4)_6$ ) showed remarkably enhanced catalytic performance for the oxidative coupling of methane (OCM) when compared with the unsubstituted strontium hydroxyapatite. Other substituted transition metals such as zinc, cobalt and nickel were not so effective for improving the catalytic performance for the OCM. The Ni-substituted catalyst exhibited quite different catalytic behavior: CO and hydrogen were the major products instead of the  $\text{C}_2$  products. The catalyst with the extent of Pb substitution ( $x$ ) of 0.2 showed the highest  $\text{C}_2$  selectivity and yield (about 47% and 17% at 1,023 K, respectively) and also exhibited quite stable behavior.

Key words: Lead-Substituted, Methane, Oxidative Coupling, Strontium Chlorapatite, Strontium Hydroxyapatite

### INTRODUCTION

Direct catalytic conversion of methane to  $\text{C}_2$  and higher hydrocarbons ( $\text{C}_{2+}$ ) by oxidative coupling of methane (OCM) is considered a potential route for the production of useful chemicals and fuels from abundant natural gas. A large number of materials, such as alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides, have so far been found to be effective in catalyzing the OCM, but more effective catalysts are still being sought [Amenomiya et al., 1990; Baek et al., 1998; Cho et al., 1998; Guo et al., 1998; Hutchings and Scurrall, 1992; Kim et al., 1997; Kim and Lee, 1993; Kim et al., 1990; Kim and Yu, 1990; Kong et al., 1999; Lee and Oyama, 1988; Lee and Oyama, 1989; Maitra, 1993; Yoon and Seo, 1996; Yoon and Tung, 1997].

The majority of the catalytic materials investigated were oxides, but recently some phosphate compounds have been reported to show good catalytic performance for the OCM: promoted sodium zirconium phosphates [Yoon and Seo, 1997], promoted strontium chlorapatite [Bae et al., 1999], promoted calcium chlorophosphate [Hong and Yoon, 2000], and lead-substituted calcium hydroxyapatite [Matsumura et al., 1995; Lee et al., 1998]. Among these, the last one appears to exhibit the best performance from the aspect of yield and stability. The other promoted catalysts contain chloride compounds, but they are relatively unstable under high reaction temperatures, and thus gradual disappearance of the chlorine in them has been reported to be the main cause of the catalyst deactivation. However, the lead substituted with the calcium in the hydroxyapatite structure seems to be quite stable [Lee et al., 1998]. On the other hand, transition-metal-substituted strontium hydroxyapatite has rarely been studied although strontium belongs to the same group as calcium. Other transition metals than lead have not been reported as the substituent yet.

Against this background, various transition-metal-substituted strontium hydroxyapatites ( $\text{Sr}_{10-x}\text{M}_x(\text{OH})_2(\text{PO}_4)_6$ ; M=transition met-

al) were investigated as the catalyst for the OCM in this work. Pb, Zn, Co and Ni, which have the most stable oxidation state of +2, were used as the substituent metals and the catalytic performance depending on the kind of the metal was compared, and then the amount of substitution was varied for the metal which showed the best results to find the optimum extent of substitution. In addition, lead-substituted strontium chlorapatite was prepared and tested for the purpose of comparison.

### EXPERIMENTAL

#### 1. Catalyst Preparation and Characterization

The hydroxyapatite catalysts were prepared from strontium nitrate [ $\text{Sr}(\text{NO}_3)_2$ , Junsei Chemical], dibasic ammonium phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ , Shinyo Pure Chemical] and metal nitrates [ $\text{Pb}(\text{NO}_3)_2$ , Syinyo Pure Chemical;  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Wako Pure Chemical;  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Wako Pure Chemical;  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Shinyo Pure Chemical]. A nearly saturated aqueous solution of dibasic ammonium phosphate was prepared and its pH was adjusted to about 10.5 by adding ammonia water (Yakuri Pure Chemical). To this solution, under nitrogen purge and vigorous stirring in a reflux flask, a nearly saturated aqueous solution of the metal nitrate, whose pH was also adjusted to about 10.5, was added, and then a nearly saturated aqueous solution of strontium nitrate of pH 10.5 was added drop by drop. After reflux at 363 K overnight, the water in the mixture was evaporated to get a thick paste and then it was dried at 383 K for 24 h in an oven in the air. The dried powder was heated at a rate of 10 K/min to 1,073 K and calcined for 2 h at that temperature. The catalyst thus prepared was named  $\text{SrMOHAp}(x)$ , where M is Pb, Zn, Co or Ni, and  $x$  denotes the extent of substitution as that in  $\text{Sr}_{10-x}\text{M}_x(\text{OH})_2(\text{PO}_4)_6$ . Except for the Pb-substituted ones,  $x$  was fixed at 0.5. For the Pb-substituted ones  $x$  was varied from 0.2 to 1.5. A catalyst which contained no transition metal was prepared and was designated as  $\text{SrOHAp}$ . Lead-substituted strontium chlorapatite catalysts were also prepared similarly, except that strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , Yakuri Pure Chemical) was used instead of strontium nitrate, and they were called  $\text{SrPbClAp}(0.5)$  and  $\text{SrPbClAp}(1.0)$ .

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In all the cases, stoichiometric amounts of the reagents were employed, that is, the atomic ratio of (Sr+M) to P was 10/6.

The fresh (before reaction) and used (after reaction) catalysts were characterized by X-ray diffraction (XRD: Mao Science, M18xHF-SRA) with the Cu K $\alpha$  line to observe the crystalline phases and energy dispersive X-ray spectroscopy (EDS: Tracor Northern, JSM-35CF) with 15 kV of applied voltage to observe the mole ratios of the elements. In EDS analysis, several particles were taken and the average value was used for the analysis.

## 2. Catalyst Performance Testing

The catalyst performance was tested by a conventional procedure with a tubular reactor. The OCM reaction was carried out in a 8-mm inside diameter quartz tube under atmospheric pressure by feeding methane, oxygen and helium as a diluent. The reactor was mounted vertically and heated with an electric furnace, and the feed gas flowed downward. The reaction temperature was measured with a thermocouple which was inserted into the catalyst bed from the top of the reactor. The following reaction conditions were employed unless otherwise specified. The reaction temperatures were 973 and 1,023 K; the partial pressures of methane and oxygen ( $p_{CH_4}$  and  $p_{O_2}$ ) were 16.5 and 8.3 kPa (0.16 and 0.08 atm) with the total gas flow rate of 100 cm<sup>3</sup> (STP)/min and the catalyst loading of 1.0 g, giving the space time of 0.6 g s/cm<sup>3</sup>. The product effluent was passed through a CaCl<sub>2</sub> trap to remove water and then analyzed by two on-line TCD-equipped gas chromatographs, one fitted with a Carboxen 1004 column (Supelco) to analyze H<sub>2</sub>, O<sub>2</sub>, CO and CH<sub>4</sub>, and the other with a Haysep Q column (Supelco) to analyze H<sub>2</sub>+O<sub>2</sub>+CO, CO<sub>2</sub>, CH<sub>4</sub> and higher hydrocarbons. For the quantitative analysis, the relative molar response factors (RMR) for TCD reported in the literature were used [Rosie and Barry, 1972]. For hydrogen, the RMR was determined by calibration for our apparatus; within a certain composition range (up to about 15% of H<sub>2</sub>) a linear relationship could be obtained and the RMR was 0.63 with respect to 100 for benzene.

## RESULTS AND DISCUSSION

### 1. XRD and EDS Results

The XRD patterns for some representative samples are shown in Fig. 1. For the other samples the patterns were similar as described below. Hexagonal Sr<sub>10</sub>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub> and hexagonal Sr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> phases were observed, and the catalysts appeared to consist mostly of the former except for the Ni-substituted catalyst. Regardless of the kind of metal substituted except for Ni, the patterns for either fresh or used samples were very similar to that for SrOHAp, and it is considered that this is because the extent of substitution is not large, as has been observed in earlier studies on Pb-substituted calcium hydroxyapatite and transition-metal-substituted calcium chlorapatite [Lee et al., 1998; Hong and Yoon, 2000]. No phases corresponding to some other transition metal compounds, such as oxides, were identified, and this indicates that the transition metals were well substituted with Sr either in the apatite or the phosphate. Little change was observed between the fresh and used samples, and this indicates that the apatite is thermally quite stable.

For the Ni-substituted catalyst, a quite different result was observed. The pattern for the fresh sample was similar to that for the other substituted catalysts. In the used sample, however, the amount

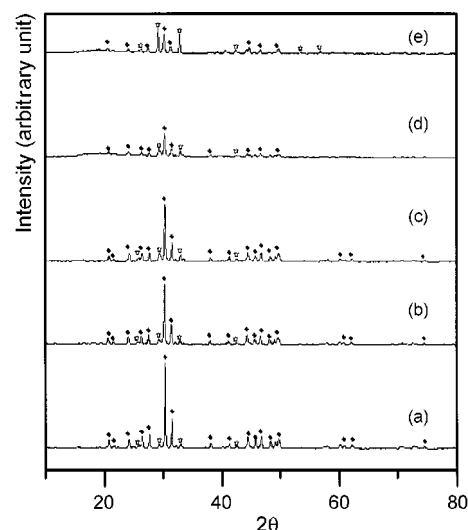


Fig. 1. X-ray diffraction patterns of selected catalysts.

◆: Sr<sub>10</sub>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>, ☆: Sr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, (a) fresh SrOHAp, (b) used SrPbOHAp(1.5), (c) used SrCoOHAp(0.5), (d) fresh SrNiOHAp(0.5), (e) used SrNiOHAp(0.5).

Table 1. EDS analysis results

Catalyst	Atomic ratio	
	Sr/P	M/(Sr+M)
SrOHAp	1.90	-
SrPbOHAp(0.2)	2.28	0.004
SrPbOHAp(0.5)	2.33	0.011
SrPbOHAp(1.0)	2.46	0.018
SrPbOHAp(1.5)	2.25	0.028
SrZnOHAp(0.5)	1.79	0.010
SrCoOHAp(0.5)	2.13	0.011
SrNiOHAp(0.5)	1.80	0.011

of the strontium phosphate phase became larger and it appears to be comparable to that of the apatite. This suggests that the presence of Ni ions tends to promote formation of the phosphate, although the reason for this is not well understood. In addition, whether the Ni is preferentially present in the apatite or in the phosphate is not also clear at the moment since both Ni and Sr have the same oxidation state of +2 and the amount of Ni added was quite small.

The XRD pattern for the Pb-substituted strontium chlorapatite was similar to that for strontium chlorapatite reported in the literature [Bae et al., 1999], and hence it was not shown here.

The EDS analysis results are shown in Table 1. The Sr/P ratios were all greater than 1.67, the theoretical ratio for the apatite. The M/(M+Sr) ratios were all smaller than the ratio employed in the preparation. This is considered to be due to the presence of another strontium compound, possibly such as SrCO<sub>3</sub>, near the surface. Since some Sr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was formed, the material balance shows that a part of the Sr will remain as an excess without forming the apatite, and hence another strontium compound should exist. Under the ambient or the reaction environment, the most probable compound is considered to be SrCO<sub>3</sub>. If so, the Sr/P ratio will come out to be greater and the M/(M+Sr) ratio to be smaller.

**Table 2. Results of the reaction at 1 h on-stream over strontium chlorapatite, strontium hydroxyapatite and lead-substituted catalysts**

Catalyst	at 973 K				at 1,023 K			
	CH <sub>4</sub> conv. (%)	C <sub>2</sub> sel. (%)	C <sub>2</sub> yield (%)	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub> conv. (%)	C <sub>2</sub> sel. (%)	C <sub>2</sub> yield (%)	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>
SrOHAp	16.0	0	0	-	19.7	4.1	0.8	0
SrClAp	3.6	0	0	-	8.4	9.7	0.8	0.53
SrPbOHAp(0.5)	28.9	37.0	10.7	1.23	38.6	40.7	15.7	1.43
SrPbClAp(0.5)	18.7	53.5	10.0	0.73	26.5	60.2	16.0	1.58
SrPbOHAp(1.0)	25.0	31.6	7.9	0.38	31.5	33.7	10.6	1.09
SrPbClAp(1.0)	14.6	51.1	7.4	0.71	25.0	57.9	14.5	1.87

## 2. Catalytic Performance

As is generally done, the selectivity to a product in this work is also defined as (the number of moles of C in that product)/(the number of moles of CH<sub>4</sub> consumed); the yield is defined as (the number of moles C in that product)/(the number of moles of CH<sub>4</sub> fed) and is equal to (the CH<sub>4</sub> conversion)×(the selectivity). The C<sub>2</sub> selectivity and yield mean the sum of selectivities and yields of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. If the terms are used without specifying any product, they mean the C<sub>2</sub> selectivity and yield. Practically no C<sub>3</sub> and higher hydrocarbons were detected in this work.

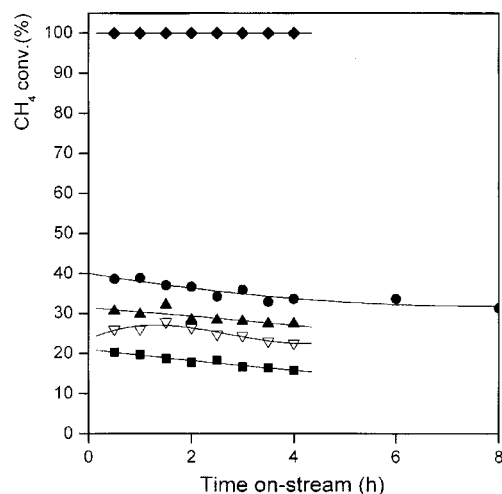
### 2-1. Effect of the Transition-Metal Substitution

The results of the reaction experiments at 1 h on-stream are shown in Table 2. Over the hydroxyapatite catalyst, SrOHAp, the C<sub>2</sub> selectivity was very low. Over the chlorapatite catalyst, SrClAp, the methane conversion became lower but the C<sub>2</sub> selectivity became higher compared with that obtained over SrOHAp. This indicates that the chlorine ion effectively suppresses the deep oxidation of hydrocarbons. Nevertheless, both catalysts are not good for the OCM, as already reported in earlier studies [Sugiyama et al., 1996; Bae et al., 1999].

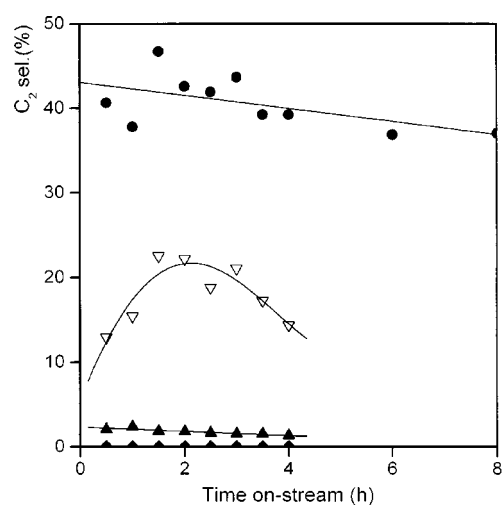
When a part of the Sr was substituted with Pb, remarkable increases in the activity and selectivity were observed for both the hydroxyapatite and chlorapatite, as shown in Table 2. Over the substituted chlorapatite the conversion was again lower, but the selectivity was higher compared with the substituted hydroxyapatite, and consequently the C<sub>2</sub> yields of the both catalysts came out to be comparable. The results in Table 2 also show that the catalytic performance depends significantly on the extent of substitution. The catalysts with the extent of substitution(x) of 0.5 exhibited better performance than those with x of 1.0.

Catalysts with different kinds of substituent transition metals were tested and their performances were compared, as shown in Figs. 2-5. In these catalysts, x was fixed at 0.5. The performance of the Pb-substituted catalyst was far superior to the others. The Zn-substituted one showed a somewhat improved performance compared with the unsubstituted one, but this is still unsatisfactorily poor. The Co-substituted one exhibited poorer performance than the unsubstituted one.

On the other hand, the Ni-substituted one showed completely different catalytic behavior. The methane conversion was near 100% and no C<sub>2</sub> products were produced. Instead, the carbon products were only CO and CO<sub>2</sub>, and majority was the former. Together with this, production of a large amount of H<sub>2</sub> with the H<sub>2</sub>/CO ratio of close to 2 was observed. Therefore, it is anticipated that one may find an application of the Ni-substituted catalyst as a good catalyst

**Fig. 2. CH<sub>4</sub> conversion vs. time on-stream at 1,023 K over transition-metal-substituted catalysts.**

●: SrPbOHAp(0.5), ▽: SrZnOHAp(0.5), ▲: SrCoOHAp(0.5), ◆: SrNiOHAp(0.5), ■: SrOHAp.

**Fig. 3. C<sub>2</sub> selectivity vs. time on-stream at 1,023 K over transition-metal-substituted catalysts.**

●: SrPbOHAp(0.5), ▽: SrZnOHAp(0.5), ▲: SrCoOHAp(0.5), ◆: SrNiOHAp(0.5).

for the selective partial oxidation or oxyreforming) of methane rather than for the OCM. The product distributions for some representative cases are presented in Table 3.

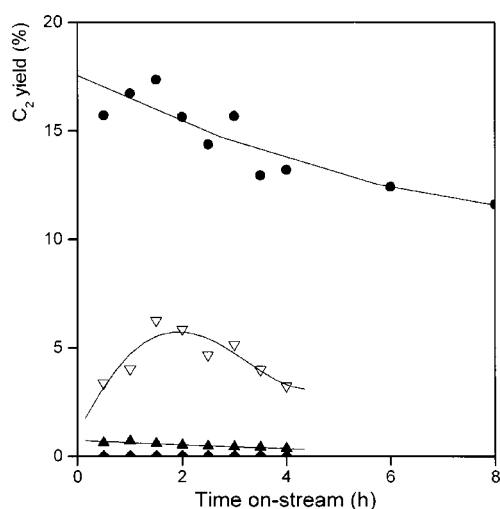


Fig. 4.  $C_2$  yield vs. time on-stream at 1,023 K over transition-metal-substituted catalysts.

●: SrPbOHAp(0.5), ▽: SrZnOHAp(0.5), ▲: SrCoOHAp(0.5), ◆: SrNiOHAp(0.5).

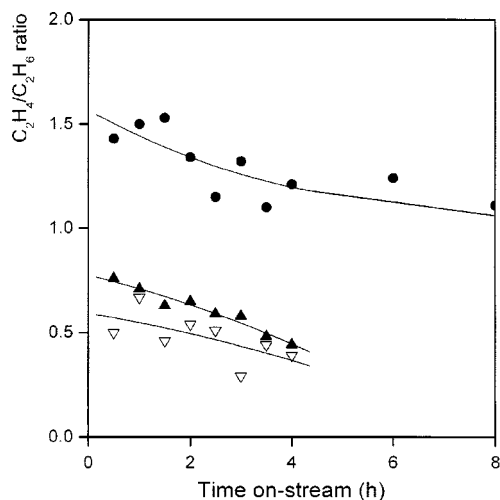


Fig. 5.  $C_2H_4/C_2H_6$  ratio vs. time on-stream at 1,023 K over transition-metal-substituted catalysts.

●: SrPbOHAp(0.5), ▽: SrZnOHAp(0.5), ▲: SrCoOHAp(0.5).

## 2-2. Effect of the Extent of Pb Substitution

The effect of the extent of substitution( $x$ ) was investigated for the Pb-substituted strontium hydroxyapatite catalyst. As shown in

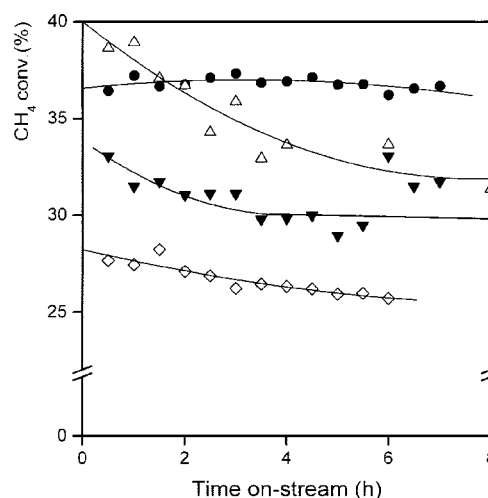


Fig. 6.  $CH_4$  conversion vs. time on-stream at 1,023 K over SrPbOHAp( $x$ ) with different  $x$ .

●:  $x=0.2$ , △:  $x=0.5$ , ▼:  $x=1.0$ , ◇:  $x=1.5$ .

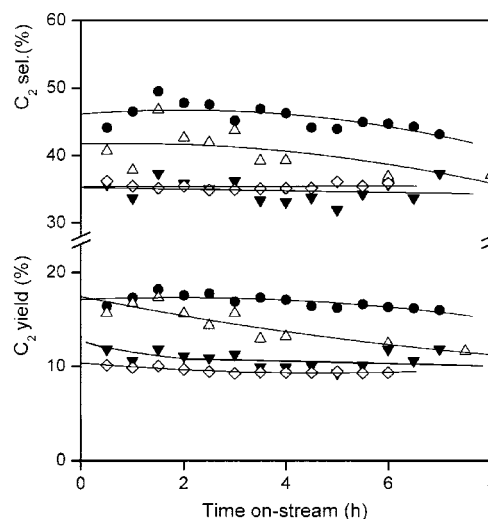


Fig. 7.  $C_2$  selectivity and yield vs. time on-stream at 1,023 K over SrPbOHAp( $x$ ) with different  $x$ .

●:  $x=0.2$ , △:  $x=0.5$ , ▼:  $x=1.0$ , ◇:  $x=1.5$ .

Figs. 6 and 7, the catalyst with  $x$  of 0.2 showed the highest  $C_2$  selectivity and yield. While the others deactivated gradually, this catalyst exhibited quite stable behavior and the  $C_2H_4/C_2H_6$  ratio was also kept almost constant at around 0.7. This result is similar to the

Table 3. Product distribution over transition-metal-substituted catalysts (reaction temp.=1,023 K, time on-stream=2 h)

Catalyst	$CH_4$ conv. (%)	Selectivity(%)				$C_2$ yield (%)	$H_2/CO$ mole ratio
		$C_2H_4$	$C_2H_6$	$CO_2$	$CO$		
SrPbClAp(0.5)	26.4	35.9	20.1	33.4	10.7	14.8	0.3
SrPbOHAp(0.5)	36.7	24.4	18.2	56.2	1.2	15.6	0.02
SrZnOHAp(0.5)	26.4	7.8	14.4	76.1	0.9	5.9	0.04
SrCoOHAp(0.5)	28.4	0.7	1.1	84.9	13.3	0.5	3.1
SrNiOHAp(0.5)	99.9	0	0	2.0	98.0	0	(~2)*

\*Due to the difficulty in quantitative determination of  $H_2$  of high composition, this is an approximate value having about 10% error.

case of the Pb-substituted calcium hydroxyapatite in earlier works where the optimum  $x$  was around 0.2-0.5 [Matsumura et al., 1995; Lee et al., 1998]. As Matsumura et al. [1995] have suggested, the presence of a proper concentration of lead would permit two stabilized methyl radicals to be found adjacent to each other and this would presumably facilitate the formation of ethane by coupling, in preference to the production of carbon oxides. In other words, relative rates of the competing reactions may be changed depending on the concentration of the lead, and thus the optimum would exist.

## CONCLUSIONS

While strontium hydroxyapatite was a poor catalytic material for the OCM, Pb-substituted strontium hydroxyapatite showed remarkably enhanced catalytic performance. Other substituted transition metals such as Zn, Co and Ni were not good for improving the catalytic performance of the OCM. The Ni-substituted catalyst exhibited quite different catalytic behavior: CO and hydrogen were the major products instead of the  $C_2$  products. The optimum extent of Pb substitution,  $x$ , was found to be around 0.2. The highest  $C_2$  selectivity and yield obtained at 1,023 K were about 47% and 17%, respectively.

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